**Supporting Information for "Prediction of the size distributions of methanol-ethanol clusters detected in VUV laser/time-of-flight mass spectrometry" (Yi Liu et. al.)**

S1. Radial distribution function (RDF) from the MD simulations in an NPT ensemble for the M1E9, M1E1, and M9E1 vapour mixtures at $1 \times P_{eq}$ and $8 \times P_{eq}$.

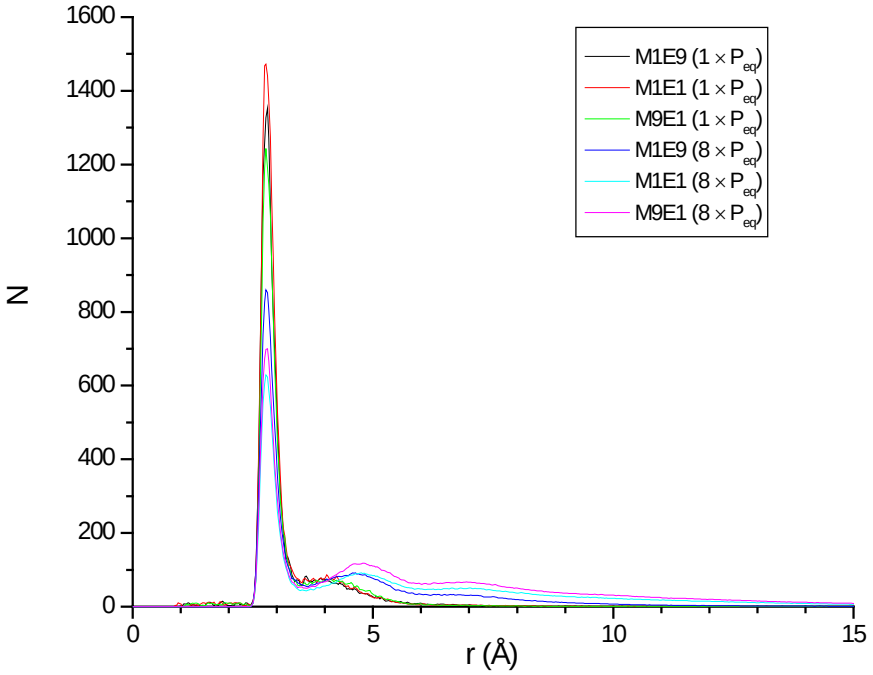
S2. Dependence of cluster size distributions for neat ethanol at $8 \times P_{eq}$ on the sphere radius used in the GCMC simulations. (a) The cluster definition based on hydrogen bond connectivity in this work; (b) The cluster definition used by Kusaka et. al. (Ref. 6-8).

S3. Size distribution of neat (a) methanol and (b) ethanol clusters at $1 \times P_{eq}$, $3 \times P_{eq}$, $6 \times P_{eq}$ and $8 \times P_{eq}$, calculated from the GCMC simulations (solid symbols). The open symbols indicate the cluster distributions at $1 \times P_{eq}$, $3 \times P_{eq}$, and $6 \times P_{eq}$ estimated from that at $8 \times P_{eq}$ using the probability-fugacity relation [Eq. (A. 1)].

S4. Size distribution of neutral methanol-ethanol clusters ($Me_mEt_n$, m+n= 3-10) calculated from the GCMC simulations for the M1E9, M1E1, and M9E1 vapour mixtures at $1 \times P_{eq}$, $3 \times P_{eq}$ and $8 \times P_{eq}$, respectively.

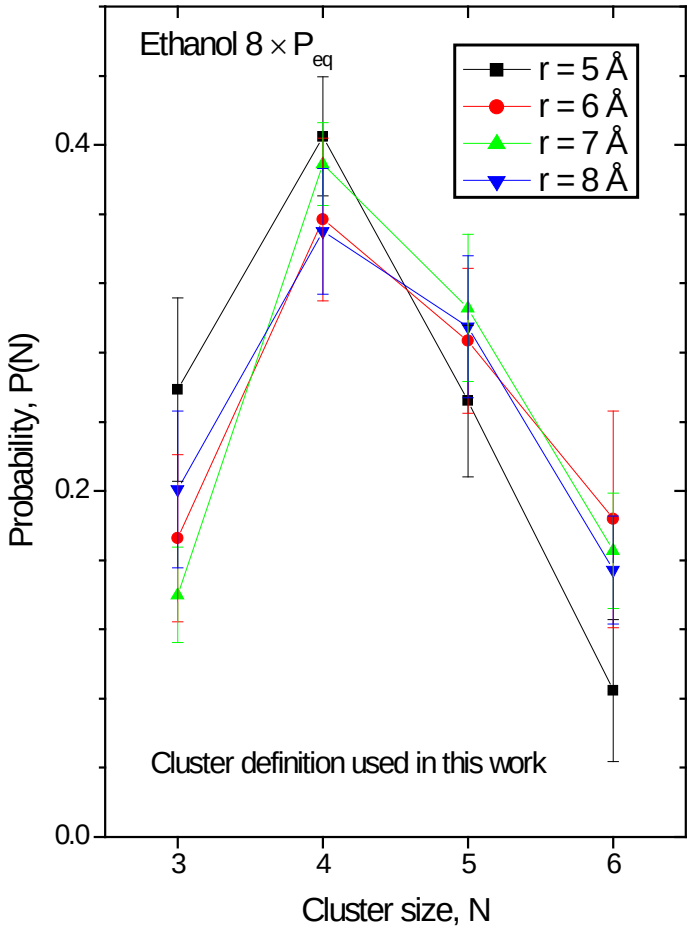
S5. Size distribution of ionized methanol-ethanol clusters ($Me_mEt_nH^+$, m+n= 2-9) estimated from the neutral cluster distribution at $8 \times P_{eq}$ calculated from the GCMC simulations using the approximations of combinatorial fragmentation process [Eq. (2)] and the probability-fugacity relation [Eq. (A. 1)] for the M1E9, M1E1, and M9E1 vapour mixtures at $12 \times P_{eq}$ or $16 \times P_{eq}$, respectively.

S6. Geometries of neutral (a) $Me_1Et_3$ and (b) $Me_3Et_1$ clusters optimized by DFT/B3LYP calculations[3]. The unit of bond length is Å, and the angles are given in degrees.

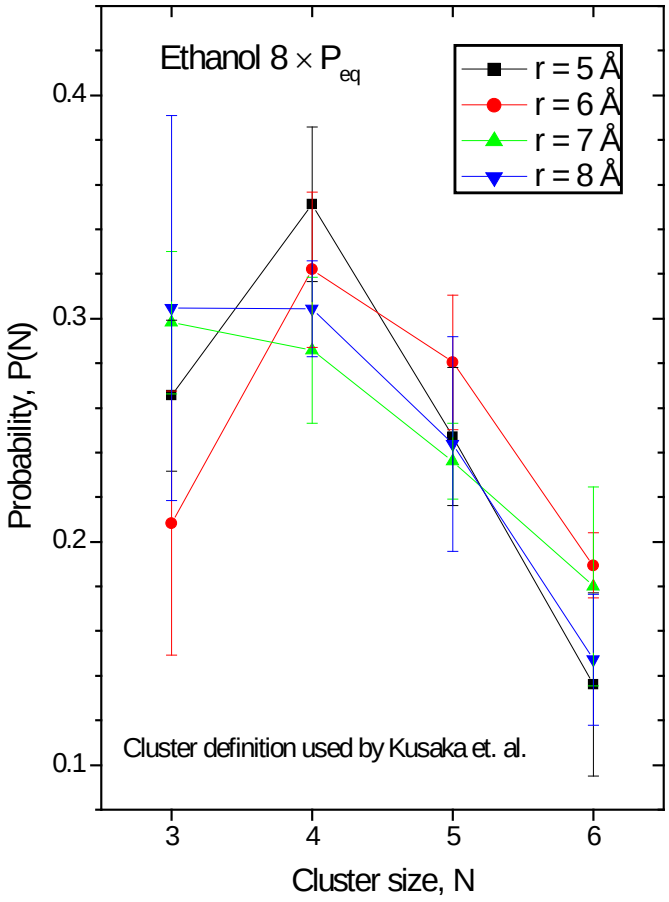



S1. Radial distribution function (RDF) from the MD simulations in an NPT ensemble for the M1E9, M1E1, and M9E1 vapour mixtures at $1 \times P_{eq}$ and $8 \times P_{eq}$.

S2 (a)

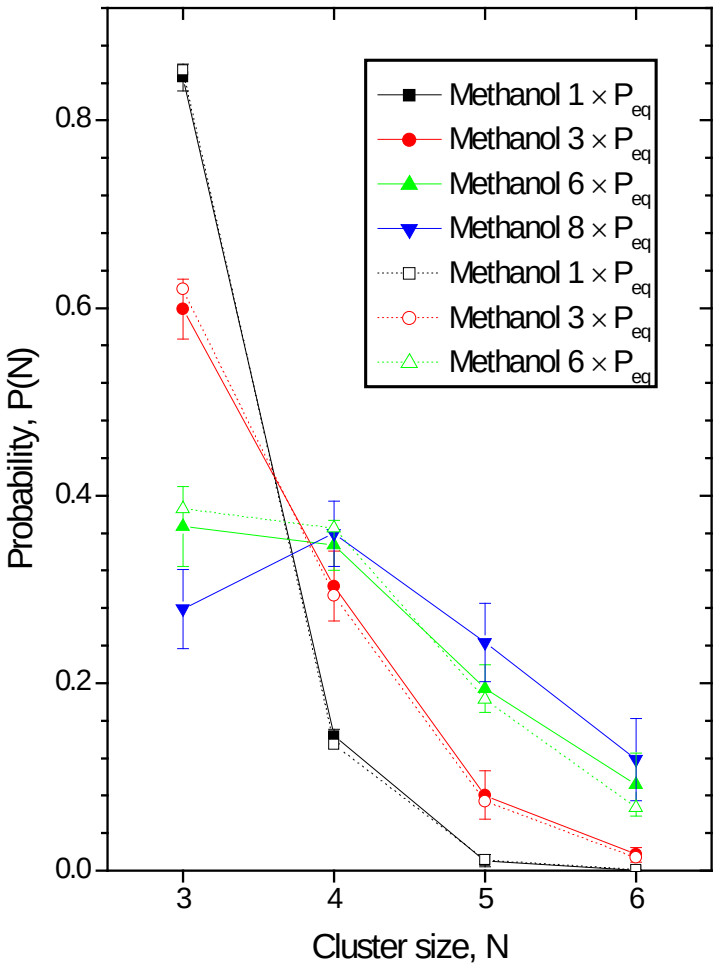

Ethanol 8 × P eq
r = 5 Å
r = 6 Å
r = 7 Å
r = 8 Å
Probability, P(N)
0.0
0.2
0.4
3
4
5
6
Cluster size, N
Cluster definition used in this work

S2 (b)

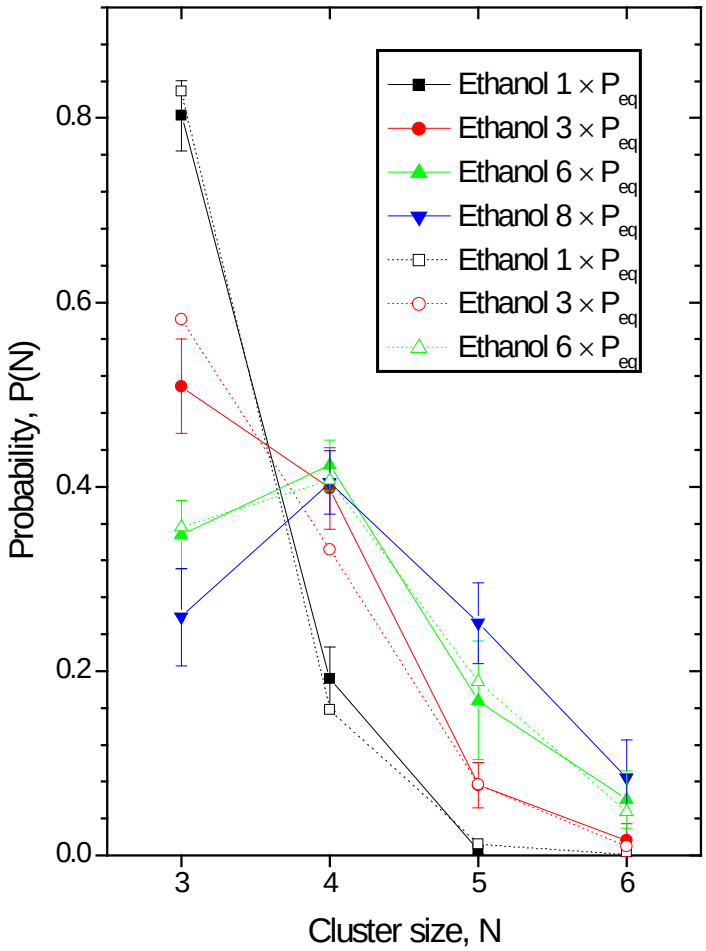



S2. Dependence of cluster size distributions for neat ethanol at 8 × $P_{eq}$ on the sphere radius used in the GCMC simulations. (a) The cluster definition based on hydrogen bond connectivity in this work; (b) The cluster definition used by Kusaka et. al. (Ref. 6-8).

S3. (a)


Methanol 1 × P_eq
Methanol 3 × P_eq
Methanol 6 × P_eq
Methanol 8 × P_eq
Methanol 1 × P_eq
Methanol 3 × P_eq
Methanol 6 × P_eq
Probability, P(N)
0.0
0.2
0.4
0.6
0.8
3
4
5
6
Cluster size, N

S3. (b)




S3. Size distribution of neat (a) methanol and (b) ethanol clusters at 1 × $P_{eq}$, 3 × $P_{eq}$, 6 × $P_{eq}$ and 8 × $P_{eq}$, calculated from the GCMC simulations (solid symbols). The open symbols indicate the cluster distributions at 1 × $P_{eq}$, 3 × $P_{eq}$, and 6 × $P_{eq}$ estimated from that at 8 × $P_{eq}$ using the probability-fugacity relation [Eq. (A. 1)].

S4. Size distribution of neutral methanol-ethanol clusters ($Me_mEt_n$, m+n= 3-10) calculated from the GCMC simulations for the M1E9, M1E1, and M9E1 vapour mixtures at $1 \times P_{eq}$, $3 \times P_{eq}$ and $8 \times P_{eq}$, respectively.

| | | | M1E9 | M1E9 | M1E9 | M1E1 | M1E1 | M1E1 | M9E1 | M9E1 | M9E1 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| m+n | m | n | $1 \times p_{eq}$ | $3 \times p_{eq}$ | $8 \times p_{eq}$ | $1 \times p_{eq}$ | $3 \times p_{eq}$ | $8 \times p_{eq}$ | $1 \times p_{eq}$ | $3 \times p_{eq}$ | $8 \times p_{eq}$ |
| 3 | 0 | 3 | 0.50 | 0.31 | 0.23 | 0.07 | 0.09 | 0.01 | 0.00 | 0.00 | 0.00 |
| 3 | 1 | 2 | 0.31 | 0.20 | 0.07 | 0.08 | 0.15 | 0.09 | 0.02 | 0.05 | 0.00 |
| 3 | 2 | 1 | 0.10 | 0.12 | 0.08 | 0.33 | 0.21 | 0.16 | 0.15 | 0.12 | 0.06 |
| 3 | 3 | 0 | 0.01 | 0.07 | 0.02 | 0.46 | 0.38 | 0.28 | 0.73 | 0.50 | 0.32 |
| 4 | 0 | 4 | 0.06 | 0.19 | 0.25 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| 4 | 1 | 3 | 0.02 | 0.04 | 0.05 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 |
| 4 | 2 | 2 | 0.01 | 0.02 | 0.02 | 0.01 | 0.03 | 0.05 | 0.00 | 0.01 | 0.00 |
| 4 | 3 | 1 | 0.00 | 0.01 | 0.00 | 0.02 | 0.03 | 0.05 | 0.01 | 0.02 | 0.04 |
| 4 | 4 | 0 | 0.00 | 0.00 | 0.01 | 0.03 | 0.07 | 0.19 | 0.09 | 0.23 | 0.33 |
| 5 | 0 | 5 | 0.00 | 0.03 | 0.16 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5 | 1 | 4 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5 | 2 | 3 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5 | 3 | 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| 5 | 4 | 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.01 |
| 5 | 5 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.09 | 0.00 | 0.05 | 0.14 |
| 6 | 0 | 6 | 0.00 | 0.01 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 6 | 1 | 5 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 6 | 2 | 4 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 6 | 3 | 3 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

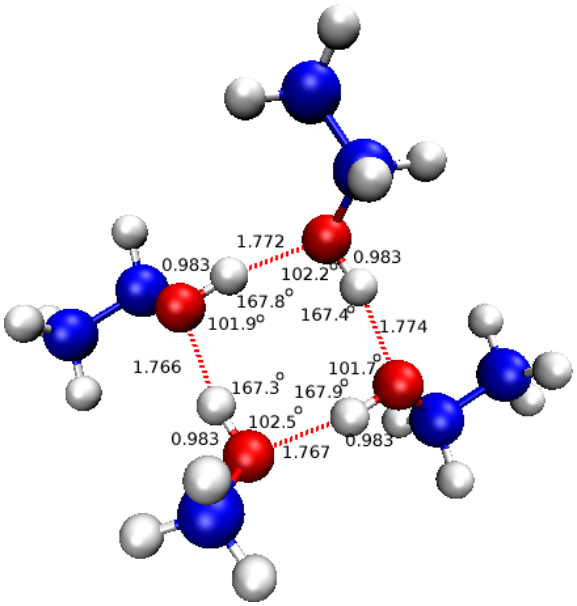
| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 4 | 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 6 | 5 | 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 |
| 6 | 6 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.01 | 0.06 |
| 7 | 0 | 7 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | 1 | 6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | 2 | 5 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | 3 | 4 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | 4 | 3 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | 5 | 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | 6 | 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | 7 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 |
| 8 | 0 | 8 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 1 | 7 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 2 | 6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 3 | 5 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 4 | 4 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 5 | 3 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 6 | 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 7 | 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 8 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |

S5. Size distribution of ionized methanol-ethanol clusters ($Me_mEt_nH^+$, m+n= 2-9) estimated from the neutral cluster distribution at $8 \times P_{eq}$ calculated from the GCMC simulations using the approximations of combinatorial fragmentation process [Eq. (2)] and the probability-fugacity relation [Eq. (A. 1)] for the M1E9, M1E1, and M9E1 vapour mixtures at $12 \times P_{eq}$ or $16 \times P_{eq}$, respectively.

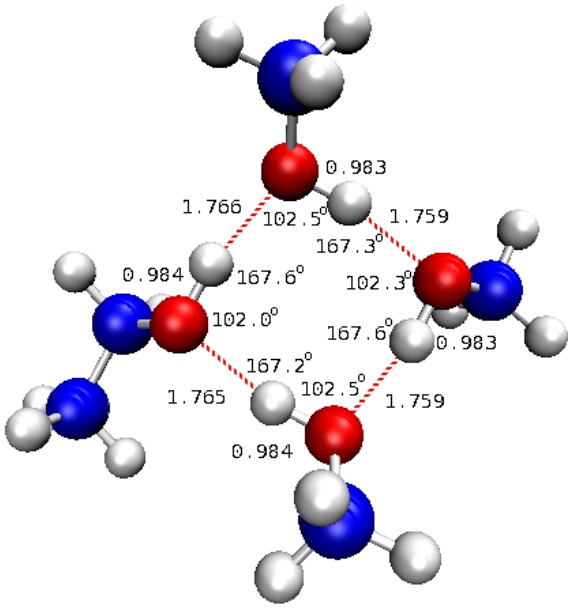
| | | | M1E9 | M1E1 | M9E1 |
|---|---|---|---|---|---|
| m+n | m | n | $12 \times p_{eq}$ | $16 \times p_{eq}$ | $12 \times p_{eq}$ |
| 2 | 0 | 2 | 0.15 | 0.02 | 0.00 |
| 2 | 1 | 1 | 0.06 | 0.09 | 0.02 |
| 2 | 2 | 0 | 0.03 | 0.17 | 0.20 |
| 3 | 0 | 3 | 0.24 | 0.01 | 0.00 |
| 3 | 1 | 2 | 0.04 | 0.03 | 0.00 |
| 3 | 2 | 1 | 0.01 | 0.07 | 0.03 |
| 3 | 3 | 0 | 0.01 | 0.21 | 0.31 |
| 4 | 0 | 4 | 0.22 | 0.00 | 0.00 |
| 4 | 1 | 3 | 0.02 | 0.00 | 0.00 |
| 4 | 2 | 2 | 0.00 | 0.01 | 0.00 |
| 4 | 3 | 1 | 0.00 | 0.04 | 0.01 |
| 4 | 4 | 0 | 0.00 | 0.20 | 0.19 |
| 5 | 0 | 5 | 0.06 | 0.00 | 0.00 |
| 5 | 1 | 4 | 0.03 | 0.00 | 0.00 |
| 5 | 2 | 3 | 0.00 | 0.00 | 0.00 |
| 5 | 3 | 2 | 0.00 | 0.01 | 0.00 |
| 5 | 4 | 1 | 0.00 | 0.02 | 0.01 |
| 5 | 5 | 0 | 0.00 | 0.08 | 0.12 |
| 6 | 0 | 6 | 0.09 | 0.00 | 0.00 |
| 6 | 1 | 5 | 0.01 | 0.00 | 0.00 |
| 6 | 2 | 4 | 0.00 | 0.00 | 0.00 |

| | | | | | |
|---|---|---|---|---|---|
| 6 | 3 | 3 | 0.00 | 0.00 | 0.00 |
| 6 | 4 | 2 | 0.00 | 0.00 | 0.00 |
| 6 | 5 | 1 | 0.00 | 0.00 | 0.00 |
| 6 | 6 | 0 | 0.00 | 0.04 | 0.07 |
| 7 | 0 | 7 | 0.02 | 0.00 | 0.00 |
| 7 | 1 | 6 | 0.00 | 0.00 | 0.00 |
| 7 | 2 | 5 | 0.00 | 0.00 | 0.00 |
| 7 | 3 | 4 | 0.00 | 0.00 | 0.00 |
| 7 | 4 | 3 | 0.00 | 0.00 | 0.00 |
| 7 | 5 | 2 | 0.00 | 0.00 | 0.00 |
| 7 | 6 | 1 | 0.00 | 0.00 | 0.00 |
| 7 | 7 | 0 | 0.00 | 0.00 | 0.03 |

S6. (a)




S6. (b)




S6. Geometries of neutral (a) $Me_1Et_3$ and (b) $Me_3Et_1$ clusters optimized by DFT/B3LYP calculations[3]. The unit of bond length is Å, and the angles are given in degrees.